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# Reference Data

## Total Assignment of the $^{1}H$ and $^{13}C$ NMR Chemical Shifts of Three Bisabolane Hydrocarbons by 2D-NMR Spectroscopy

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Three known bisabolane hydrocarbons, *α-trans*-bergamotene, sesquiphellandrene and zingiberene, were isolated from the aerial parts of *Alpinia densibracteata*. Their $^{1}H$ and $^{13}C$ NMR spectra were completely assigned by using a combination of $^{13}C$ DEPT and 2D-NMR experiments ($^{1}H$–$^{1}H$ COSY, single-bond $^{13}C$–$^{1}H$ correlation, long-range $^{13}C$–$^{1}H$ correlation and INADEQUATE). © 1997 by John Wiley & Sons, Ltd.

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KEY WORDS NMR; $^{13}C$ NMR; $^{1}H$ NMR; bisabolane sesquiterpene; *Alpinia densibracteata*; 2D homonuclear and heteronuclear correlations; 2D-INADEQUATE

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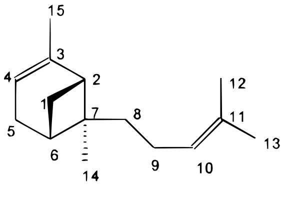
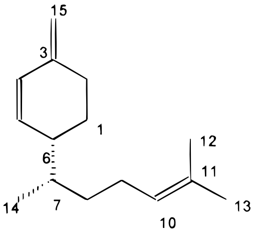
## INTRODUCTION

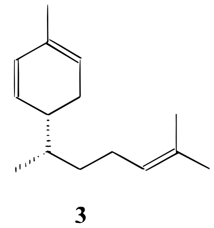
During the course of our investigations of *Alpinia densibracteata* T. L. Wu and Senjen, we isolated three bisabolane sesquiterpene hydrocarbons, *α-trans*-bergamotene (**1**), sesquiphellandrene (**2**) and zingiberene (**3**). Full $^{13}C$ and partial $^{1}H$ data have been reported[1] for **1** but no assignments have been given. Fully assigned $^{13}C$ and partial $^{1}H$ data have been suggested[2] for **2**, but published NMR assignments[3] for the closely related compounds **3** seemed to be inconsistent with those for **2**. We therefore decided to undertake a detailed NMR study of **1**–**3** utilizing a range of 1D ($^{1}H$, $^{13}C$ and $^{13}C$ DEPT) and 2D ($^{1}H$–$^{1}H$ COSY, single-bond $^{13}C$–$^{1}H$ correlation,[4] long-range $^{13}C$–$^{1}H$ correlation and INADEQUATE) experiments.



**1**



**2**



**3**

## EXPERIMENTAL

All NMR spectra were recorded on a Bruker DRX-500 spectrometer in $CDCl_3$ solutions; tetramethylsilane (TMS) was used as an internal standard. Resonance multiplicities for $^{13}C$ were established via the acquisition of DEPT spectra. For the DEPT sequence,[5] the width of a $^{13}C$ 90° pulse was 5.5 µs, that of a $^{1}H$ 90° pulse was 8.2 µs and the $(2J)^{-1}$ delay was set at 3.4 ms.

The homonuclear $^{1}H$–$^{1}H$ shift correlated two-dimensional diagrams were obtained using the COSY-45 pulse sequence.[6,7] The spectral widths were 4000 Hz; spectra were collected as 1024 × 256 blocks of data and were processed by sinusoidal multiplication in each dimension, followed by symmetrization of the final data matrix. Other parameters were as follows: number of increments in $t_1$, 256; number of scans, 16; phase cycling, 16; and relaxation delay, 2 s.

The heteronuclear 2D $^{13}C$–$^{1}H$ chemical shift correlation experiments were carried out with proton decoupling in the $F_1$ dimension.[8] The spectra were acquired with 1024 × 256 data points. Spectral widths of 20 000 and 4000 Hz were employed in the $F_2$ ($^{13}C$) and $F_1$ ($^{1}H$) domains, respectively. Data were processed by exponential multiplication (LB = 3 Hz) in $F_2$ and sinusoidal multiplication in $F_1$, and zero-filling was applied in $F_1$. The mixing delay for single-bond correlations was 3.4 ms, whilst for long-range (2/3) bond correlations it was 50 ms, the relaxation delay was 1.5 s and 16 phase-cycling steps were employed.

The 2D $^{13}C$–$^{13}C$ double quantum coherence spectra[9,10] were acquired using a Bruker 2.5 mm dual probe ('microprobe:' sample size *ca.* 50 mg; sample volume *ca.* 200 µl). Spectral widths of 20 000 Hz, a 32-step phase cycling and a data acquisition matrix of 8192 × 256 data points were used. Data files were processed using sinusoidal multiplication in both dimensions. The delay for the creation of the double quantum coherence was 6.25 ms (corresponding to a coupling of 40 Hz), and the relaxation delay was 4 s.

## RESULTS AND DISCUSSION

Fully assigned carbon and proton chemical shifts for **1**–**3** are given for the first time in Tables 1 and 2, respectively. Assignments of chemical shifts for the carbon skeleton were made by analysis of INADEQUATE spectra and assignments of attached protons was then achieved by analysis of single-bond $^{13}C$–$^{1}H$ correlation spectra. The results from long-range $^{13}C$–$^{1}H$ correlation experiments and $^{1}H$–$^{1}H$ COSY were also consistent with the assignments in Tables 1 and 2.

Our analysis suggests that $^{13}C$ and partial $^{1}H$ data given in the literature for **2** were mostly correctly assigned,[2] whereas $^{13}C$ and $^{1}H$ assignments for **3** contained many errors.[3]

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Table 1. $^{13}$C NMR chemical shifts of bisabolanes 1–3

| Assignment | 1 | 2 | 3 |
|---|---|---|---|
| 1 | 31.6 | 24.5 | 24.5 |
| 2 | 45.5 | 30.4 | 120.4 |
| 3 | 144.5 | 143.7 | 131.0 |
| 4 | 116.5 | 129.6 | 127.9 |
| 5 | 31.3 | 135.1 | 131.0 |
| 6 | 39.1 | 40.7 | 38.1 |
| 7 | 41.2 | 36.7 | 36.1 |
| 8 | 38.7 | 34.4 | 34.3 |
| 9 | 23.8 | 26.1 | 26.0 |
| 10 | 125.3 | 124.8 | 124.9 |
| 11 | 130.9 | 131.1 | 131.1 |
| 12 | 17.6 | 17.7 | 17.7 |
| 13 | 25.7 | 25.7 | 25.7 |
| 14 | 17.5 | 15.9 | 16.6 |
| 15 | 23.0 | 110.0 | 21.1 |

Table 2. $^{1}$H NMR chemical shifts of bisabolanes 1–3

| Assignment | 1 | 2 | 3 |
|---|---|---|---|
| 1 | 2.31, 1.17 | 1.70, 1.41 | 2.02, 2.02 |
| 2 | 2.01 | 2.41, 2.29 | 5.42 |
| 4 | 5.20 | 6.12 | 5.57 |
| 5 | 2.25, 2.13 | 5.56 | 5.61 |
| 6 | 2.15 | 2.21 | 2.29 |
| 7 |  | 1.55 | 1.56 |
| 8 | 1.66, 1.66 | 1.40, 1.21 | 1.40, 1.21 |
| 9 | 1.98, 1.98 | 2.03, 1.92 | 2.03, 1.92 |
| 10 | 5.16 | 5.09 | 5.09 |
| 12 | 1.62 | 1.59 | 1.59 |
| 13 | 1.70 | 1.67 | 1.67 |
| 14 | 0.83 | 0.84 | 0.86 |
| 15 | 1.66 | 4.73, 4.71 | 1.70 |

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